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Preliminary communication

ISOCYANIDE INSERTION INTO PLATINUM—OXYGEN BONDS

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Summary

The reaction of isocyanides, CNR, with hydroxy- and methoxy-alkyl complexes of platinum(II), $PtOH(R)(Ph_2PCH=CHPPh_2)$ and $PtOCH_3(R)(Ph_2PCH=CHPPh_2)$ ($R = CF_3, CH_2CN$) affords insertion products $Pt(CONHR)(R)(Ph_2PCH=CHPPh_2)$ and $Pt[C(OCH_3)=NR](R)(Ph_2PCH=CHPPh_2)$ containing the carboxamido and imidoyl moiety, respectively.

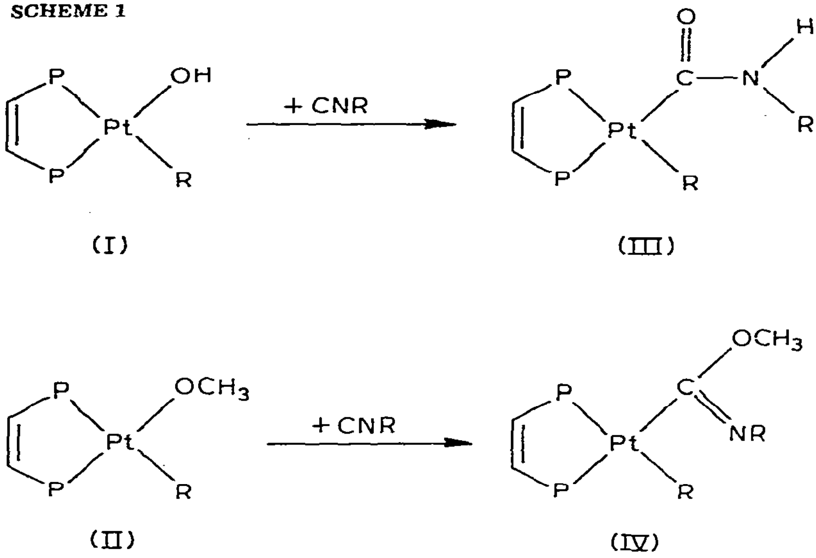
The reactions of isocyanides with transition metal complexes having M—H, M—C or M—Cl bonds give a variety of novel insertion and addition products [1—4]. To date no example of an isocyanide insertion reaction into M—O bonds has been reported, although some insertions of molecules such as CO [5—7], CO_2 [8], COS [8] and SO_2 [9] are known to take place.

Following studies [7,10—12] on the reactivity of Pt—OH and Pt—OCH_3 bonds towards small molecules and the condensation reactions with weak carbon or nitrogen acids, we have now found that the insertion reactions of isocyanides occur with complexes I and II yelding carboxamido III and *N*-(alkyl- or aryl-)methoxyimidoyl (IV) derivatives, respectively (Scheme 1).

A typical procedure consists of stirring a suspension of I or II in n-heptane with the stoichiometric amount of CNR under N_2 at room temperature for 24 h. The white products are filtered off, washed with heptane and recrystallized from CH_2Cl_2/Et_2O (yeld 40—70%). Complexes III and IV are soluble in dichloromethane and chloroform and insoluble in ether and hydrocarbons. Elemental analyses for these complexes agree with the calculated values; ^1H NMR and IR data are reported in Table 1.

The solid state IR spectra of complexes III show a weak band due to $\nu(NH)$ around 3400 cm^{-1} and strong absorptions due to $\nu(C=O) + \delta(NH)$ between

SCHEME 1



R = CF_3 , CH_2CN ; P⌒P = *cis*-$Ph_2PCH{=}CHPPh_2$;

R = methyl ; *p*-methoxyphenyl ; 2,6-dimethylphenyl

TABLE 1

SELECTED ^{1}H NMR AND IR DATA FOR CARBOXAMIDO- AND *N*-(ALKYL- OR ARYL-)METHOXYIMIDOYL DERIVATIVES

Compound	Chemical shift, δ (ppm)[a]		IR (Nujol (cm^{-1}))
	CH_3 or [NH]	CH_2CN	
$Pt(CONHCH_3)(CF_3)(P{-}P)$ (IIIa)	2.49(d), ^3J(HNCH) 4.5 Hz ^4J(PtCNCH) ≅ 6 Hz [4.97(br)]	—	3450w ν(NH) 1593s, 1576vs ν(C=O)+ δ(NH)
$Pt[CONHC_6H_3(CH_3)_2](CF_3)(P{-}P)$ (IIIb)	1.81(s) [6.62(br)]	—	3415w ν(NH) 1607vs, 1585s, 1572s ν(C=O)+ δ(NH)
$Pt(CONHC_6H_4OCH_3)(CH_2CN)(P{-}P)$ (IIIc)	3.67(s) [6.60(s)]	2.01(t), ^3J(PPtCH) 7.9 Hz ^2J(PtCH) 99.5 Hz	3415w ν(NH) 2200s ν(C≡N) 1620vs, 1587m ν(C=O)+ δ(NH)
$Pt[C(OCH_3){=}NCH_3](CH_2CN)(P{-}P)$ (IVa)	2.64(s)[b], ^4J(PtCNCH) 7.7 Hz 3.54(s)[c], ^4J(PtCOCH) 5.2 Hz	1.76(dd), $^3J(PPtCH)_{cis}$ 7.4 Hz $^3J(PPtCH)_{trans}$ 8.8 Hz ^2J(PtCH) 96.5 Hz	2206s ν(C≡N) 1600vs ν(C=N)
$Pt[C(OCH_3){=}NC_6H_4OCH_3]$- $(CH_2CN)(P{-}P)$ (IVb)	3.58(s)[c], ^4J(PtCOCH) ≅ 4.2 Hz 3.69(s)[d]	1.53(dd), $^3J(PPtCH)_{cis}$ 6.9 Hz $^3J(PPtCH)_{trans}$ 8.6 Hz ^2J(PtCH) 96.8 Hz	2201s ν(C≡N) 1555s ν(C=N)

[a] Measured in $CDCl_3$ (IIIa—IIIc), in CD_2Cl_2 (IVa, IVb). [b] $=N{-}CH_3$. [c] $C{-}O{-}CH_3$. [d] $PhOCH_3$.

1550—1620 cm^{-1}. These assignements are in agreement with those previously reported for analogous carboxamidoplatinum(II) complexes obtained by different methods [13]. The ^{1}H NMR spectra of complexes III are characterized by the broad NH signal and the methyl resonance of the carboxamido group. In particular, the methyl resonance of IIIa is split into a doublet due to the coupling with the NH proton; on addition of D_2O this doublet changes into a singlet, owing to NH/ND exchange.

Compounds IV show a strong absorption in the 1550—1600 cm^{-1} range due to ν(C=N) of the $C(OCH_3)=NR$ moiety [1,14,15]; in the ^{1}H NMR spectra methyl proton resonances appear as singlets with ^{195}Pt satellites.

Work is in progress to investigate the stereochemistry of the insertion products and the possible mechanisms of their formation.

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